



APPLICATION OF NANO PARTICLES FOR DYES DECOLORIZATION USING BIOSYNTHESIS OF TITANIUM OXIDE NANO PARTICLES

Dr. CH. A. I. Raju¹ | R. Mahalakshmi Kalyani² | K. Satyanandam³ | K. Prem³

¹ Assistant professor, Dept of Chemical Engineering, A. U. College of Engg., Visakhapatnam, India – 53000.

² P.G. Student, Department of Chemical Engineering, A. U. College of Engg., Visakhapatnam, India – 530003.

³ Research Scholar, Dept of Chemical Engg, A. U. College of Engg., Visakhapatnam, India – 530003.

ABSTRACT

Plenty and pretty applications of nano particles have gained utmost priority now a days due to their versatile flexibility in wide range of applications.. In the present research, experiments were carried out using Titanium dioxide nano particles for dyes decolorization using AntigognonLeptopus leaves by Biosynthesis Process. The variables incorporated in the present study are Contact time, pH, initial Concentration of Dyes, Dosage of nano particle solution and temperature. The characterization studies were carried out using XRD and FTIR. The dyes considered for the present study are Solo Chrome Black(SCB), Titan Yellow(TY), Bromo Thymol Blue(BTB), Bromo Cresol Purple(BCP). The Optimum pH for SCB-4, TY-5, BTB-6 and BCP-7. The Positive Results confirmed that antigognonLeptopus Leaves broth combined with Titanium dioxide solution formed Titanium Nano Particles and it is capable of removing dyes.

KEYWORDS: FTIR, pH, Dyes, Dosage, XRD, Concentration.

Introduction

The name and fame of nano particles has reached pinnacle due to its versatile and flexibility in applications. The maximum attention has turned towards nano particles for degradation of waste waters due to their high surface area and high stability [01–09]. The metal oxide nano particles produced from biosynthesis have gained much importance and are widely used for decolorization of dyes waste waters due to low cost, ecofriendly nature and non-toxicity [10, 11]. Hence an attempt is made for dyes decolorization using titanium nano particles obtained from biosynthesis using antigognonleptopus leaves.

Materials and Methods:

The present experimentation is carried out in batch process, for removal of dyes (Solo Chrome Black–SCB, Titan Yellow–TY, Bromo Thymol Blue–BTB, Bromo Cresol Purple–BCP) from aqueous solutions by using AntigognonLeptopus leaves with Titanium nano particles (al-ti-nps)



Fig. 1. Dyes

Analytical grade chemicals were used for experimentation and need no further purification. Double distilled water is used to prepare all stock and synthetic solutions. From a stock solution containing 1000 mg of dyes in 1.0 litre, the synthetic solutions of dyes were made. By addition of 0.1 M HCl and 0.1 M NaOH solutions the pH of dyes solutions were adjusted to the desired value.

Preparation of the Broth solutions and Nano particles formation:

Preparation of AntigognonLeptopus broth :

In this process 10 gm of fresh and cleaned leaves of AL are taken in a magnetic stirrer and to this 110 ml of distilled water is added and it is heated at 60°C for 10 min. After that the solution is filtered in 250 ml conical flask using whatmann's filter paper and it is kept aside for further process. The broth obtained is in pale yellow colour

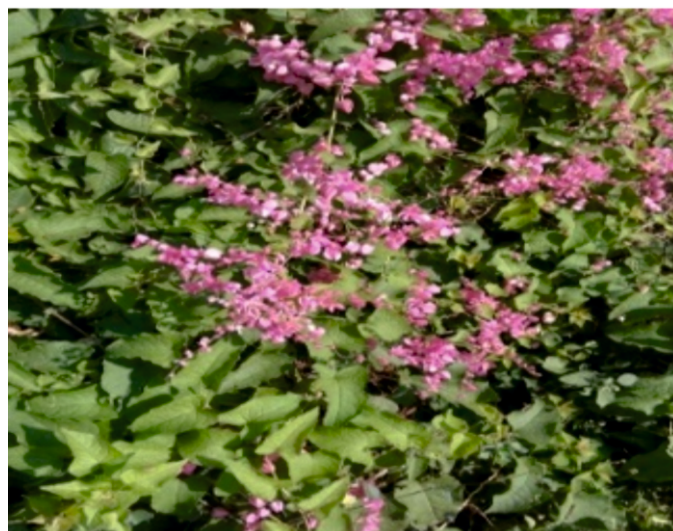


Fig.2 AntigognonLeptopus Leaves

Preparation of Nano Particles:

In this process 10 ml of broth solution is taken and to that 90 ml of TiO₂ is added in a 250 ml conical flask and is kept in an orbital shaker for 24 Hrs in order to obtain nano particles. The nano particles formation is noticed when the pale yellow color is changed to White color. This solution is used for various dyes degradation process of different concentrations and different dosages.



Fig. 3 Nano particles solutions for AntigognonLeptopus

Characterization Studies:

Characteristic studies were carried by XRD and FTIR.



Fig. 4 Centrifuge samples for drying and Characterization analysis (FTIR & XRD)

Results and Discussions:**CHARACTERIZATION.****FTIR Spectrum**

The FTIR spectrum of TiO₂ nanoparticles is shown in Figure 5 with the broth antigenonleptopus. The fundamental mode of vibration for Antigononleptopus Broth at 3411.26 which correspond to the N-H Bending from Amines, 3293.59 which correspond to the C-H Stretch from alkane, 2851.88 which corresponds to C-H Stretch from alkane. 1634.74 which correspond to N-H bending from amine. 1010.74, 1017.49, 1067.65, 1125.51, 1221.96, 1232.57, 1277.90, 1383.96 which corresponds to C-F Stretch Alkyl Halides. 930.69, 938.41, 976.99 which corresponds to =C-H bending from Alkenes. 602.78, 633.64, 640.39, 649.07, 652.58, 668.36, 673.19, 696.33, 706.94, 734.91, 742.63, 768.67 which corresponds to C-Cl stretch from alkyl halides[12-16].

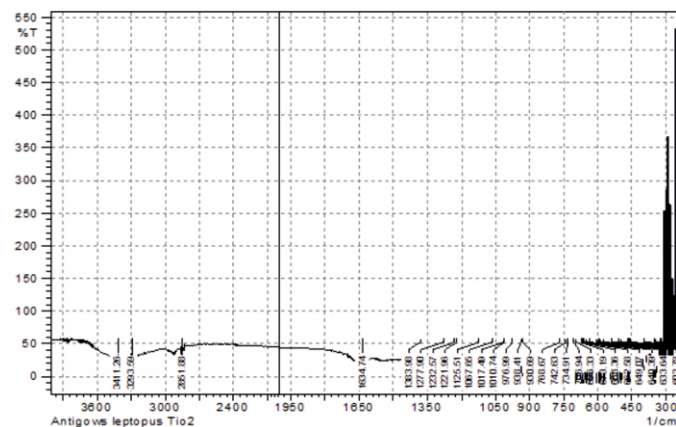


Fig.5FTIR Spectrum of Antigononleptopus Titanium nano particles

X-Ray Diffraction

Fig. 6 shows the XRD for the Titanium nanoparticles using Antigononleptopus broth. The peaks at 2θ values of 0.9641, 0.8866, 0.7709 and 0.5357 corroborate Cd₂O₆ FCl₄4O₁₄P₄, KLiO₄S, AuCSand F₂O₂Ti. Their corresponding d-values are 12.0065, 3.9861, 4.2468, and 1.700 respectively[12,17-20].

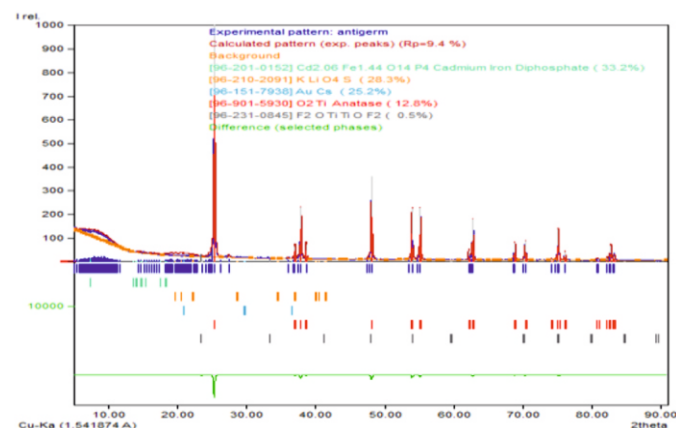


Fig. 6 XRD pattern of Antigononleptopus Titanium nano particles.

Effect of contact time

The Decolourization of Dyes(Solo Chrome Black–SCB, Titan Yellow–TY, Bromo Thymol Blue–BTB, Bromo Cresol Purple–BCP) was studied as a function of contact time at Room temperature. 20 ml of 20 mg/L Dye solution was taken with 5 ml of Antigononleptopus broth Titanium nano particles (al-ti-nps) solution at different time intervals ranging from 1 hr to 72 hrs. At the start, the ions adsorbed and occupied selectively the active sites on the al-ti-nps solution. As the contact time increased the active sites on the al-ti-nps were filled. The rate of adsorption became gradually slower and reached an exhaust stage, resulting constant value. The results obtained are shown in figure 7. As a result of the experiment, the highest % Removed for the Dyes (SCB, TY, BTB, BCP) was 53%, 54%, 48%, 47% at the time of 18 Hrs, 24 Hrs, 16 Hrs, 20 Hrs. [21-25].

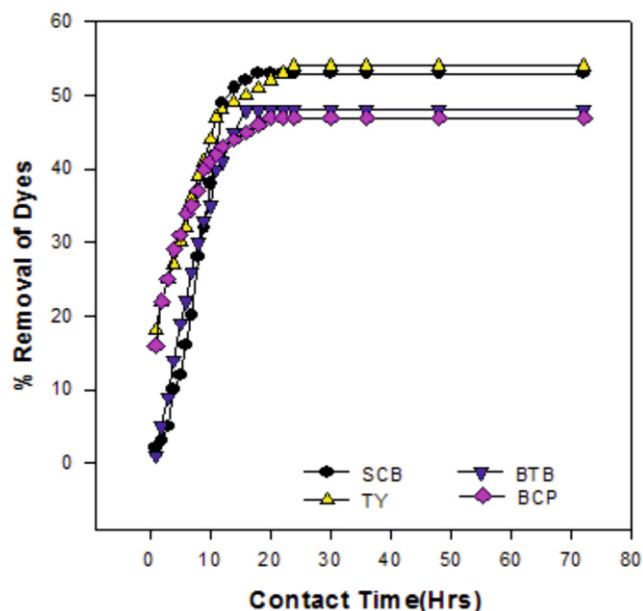


Fig. 7 Effect of Contact time for % Removal for AL

Effect of pH

In order to find the effect of pH on Dye Decolourization using the Antigononleptopus, experiments have been carried out at various initial pH values and results are given in figure 8. The removal was increased from 22% to 59% as pH was increased from 2 to 8, the pH is varied for every dye used with the broth solution Antigononleptopus whereas further increase in pH had a negative effect. The maximum % removal was found to be 53% at pH 4 for SCB Dye, 59% at pH 5 for TY dye, 56% at pH 6 for BTB dye, 51% at pH 7 for BCP dye [26-30].

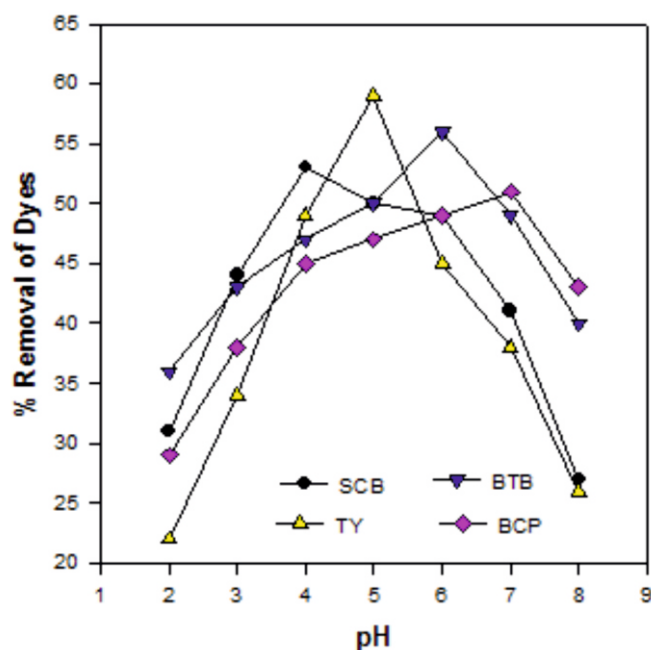


Fig. 8 Effect of pH for Antigononleptopus leaves

Effect of Concentration:

The percentage Removal of dyes at various initial concentrations is depicted in Fig. 9. At concentration of Dye solution (20 mg/L), maximum % removal is obtained and is different for every Dye using Broth Antigononleptopus and on

further increase in concentration (200 mg/L), %removal has been decreased. This is due to higher interaction between AntigononLeptopus Broth and the Dye solution. The maximum removal of SCB Dye is 56%, TY dye is 62%, BTB dye is 64%, BCP is 59 % [31-35].

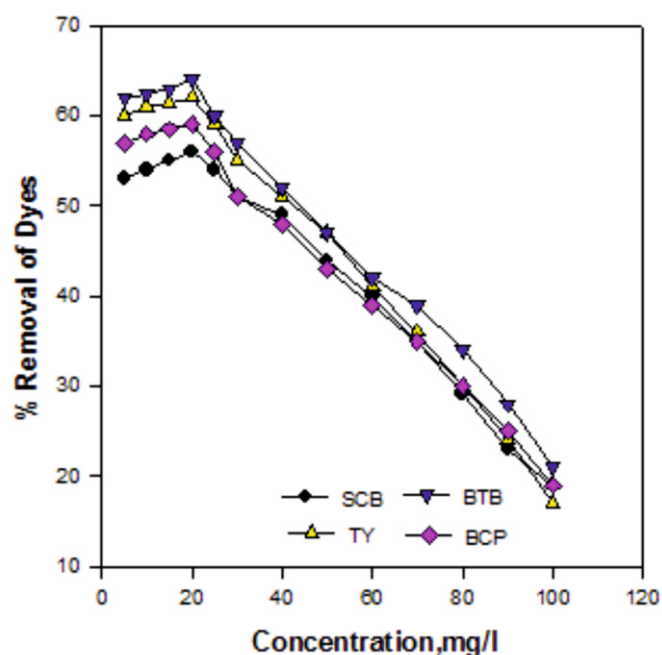


Fig. 9 Effect of Concentration for AntigononLeptopus leaves

Effect of Dosage:

The variation of % removal of Dyes (SCB, TY, BTB, BCP) was studied using different dosages of the broth AntigononLeptopus. Results from the fig 10 showed that % removal of Dyes (SCB, TY, BTB, BCP) increased. The maximum % removal is attained at 11 ml and was almost constant at higher dosages. This trend could be explained as a consequence of partial aggregation. Therefore, the optimum dosage was selected as 11 ml for further experiments. The maximum % removal of SCB dye is 76%, TY dye is 86%, BTB dye is 75%, BCP dye is 68%. This trend can be predicated to larger surface area and availability of more sorption site [36-40].

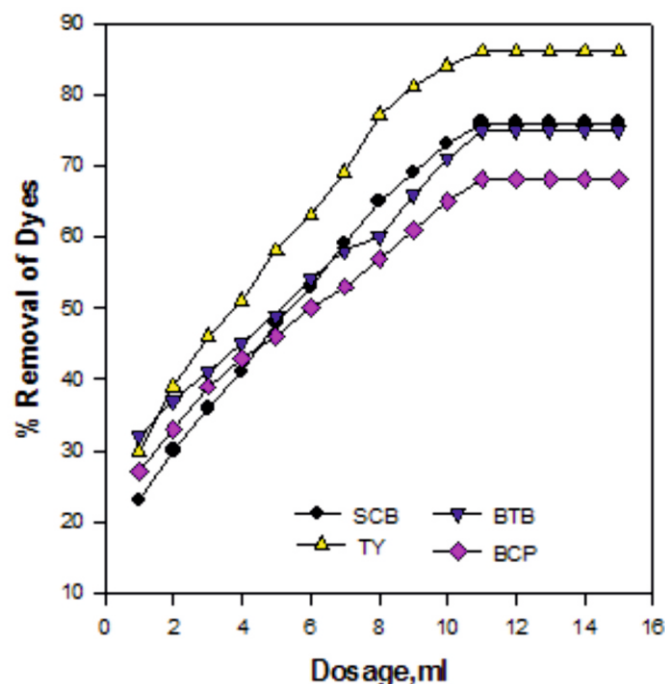


Fig. 10 Effect of Dosage for AntigononLeptopus leaves

Effect of temperature

The dependence of temperature on the % removal of dyes is investigated at different temperatures as given in fig. 11. Results showed that %removal of Dyes (SCB, TY, BTB, BCP) increased from 54% to 89% with increase in temperature from 283 K to 323 K. This indicates that the % removal of Dyes using Broth AntigononLeptopus was controlled by an endothermic process. The increase in removal with temperature may be attributed to either increase in the number of

active surface sites available for interaction on the Dyes. The maximum % removal of SCB dye is 83 %, TY dye is 89%, BTB dye is 84 %, BCP is 83 % [41-45].

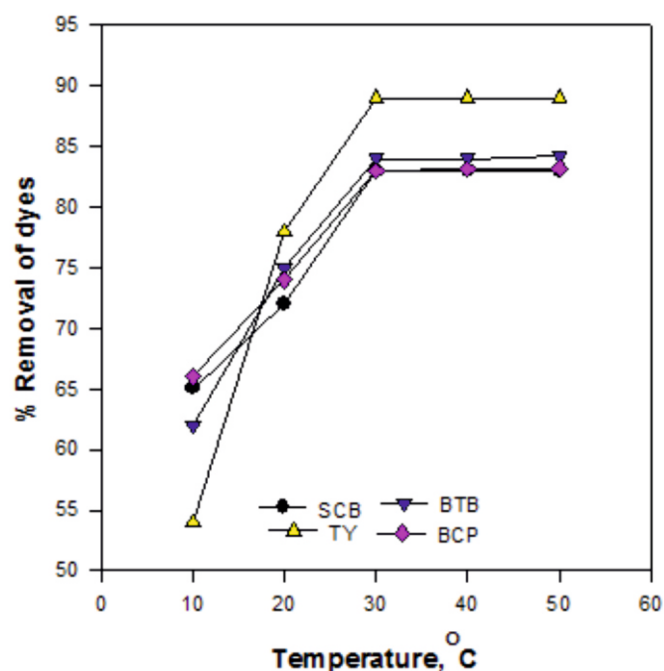


Fig. 11 Effect of Temperature for AntigononLeptopus leaves

Conclusions:

The analysis of the experimental data result in the following conclusions:

- 1) The maximum dye decolourization of solo chrome black dye onto AntigononLeptopus leaves with Ti-nano solution observed when the processing parameters are set as: $t = 18$ Hrs, $pH = 4$, $w = 11$ ml, $Co = 20$ mg/L and $T = 303$ K. is 83%.
- 2) The maximum dye decolourization of Titan yellow dye onto AntigononLeptopus leaves with Ti-nano solution observed when the processing parameters are set as: $t = 24$ Hrs, $pH = 5$, $w = 11$ ml, $Co = 20$ mg/L and $T = 303$ K is 89%.
- 3) The maximum dye decolourization of Bromothymol blue dye onto AntigononLeptopus leaves with Ti-nano solution observed when the processing parameters are set as: $t = 16$ Hrs, $pH = 6$, $w = 11$ ml, $Co = 20$ mg/L and $T = 303$ K is 84%.
- 4) The maximum dye decolourization of Bromo cresol purple dye onto AntigononLeptopus leaves with Ti-nano solution observed when the processing parameters are set as: $t = 20$ Hrs, $pH = 7$, $w = 11$ ml, $Co = 20$ mg/L and $T = 303$ K is 83%.

With the above conclusions the authors confirm that the above mentioned leaves are capable of removing dyes.

Acknowledgements

The Authors expresses their deep sense of gratitude to Andhra University and Department of Chemical Engineering for providing chemicals, equipment and laboratory facilities. The Authors also expresses their sincere thanks to DST-PURSE programme, Andhra University, Visakhapatnam and Advanced Analytical Laboratory for carrying out characterization (XRD and FTIR).

References

- [1] M.Y. Nassar, "Size-controlled synthesis of $CoCO_3$ and Co_3O_4 nanoparticles by free-surfactant hydrothermal method", *Mater. Lett.*, 94 (2013), pp. 112–111 Article PDF (510 K) Citing articles (23)
- [2] M.Y. Nassar, A.S. Attia, K.A. Alfallos, M.F. El-Shahat, "Synthesis of two novel dinuclear molybdenum(0) complexes of quinoxaline-2,3-dione: new precursors for preparation of α - MoO_3 nanoplates", *Inorg. Chim. Acta*, 405 (2013), pp. 362–367 Article View Record in Scopus Citing articles (9)
- [3] M.Y. Nassar, T.Y. Mohamed, I.S. Ahmed One-pot solvothermal synthesis of novel cobalt salicylaldehyde-urea complexes: a new approach to Co_3O_4 nanoparticles *J. Mol. Struct.*, 1050 (2013), pp. 81–87
- [4] M.Y. Nassar, M.M. Moustafa, M.M. Taha Hydrothermal tuning of the morphology and particle size of hydrozincite nanoparticles using different counterions to produce nanosized ZnO as an efficient adsorbent for textile dye removal *RSC Adv.*, 6 (2016), pp. 42180–42195
- [5] T. Jiao, Y. Liu, Y. Wu, Q. Zhang, X. Yan, F. Gao, A.J.P. Bauer, J. Liu, T. Zeng, B. Li, "Facile and scalable preparation of graphene oxide-based magnetic hybrids for fast and

- highly efficient removal of organic dyes", *Sci. Rep.*, 5 (2015), p. 12451
- [6] H. Guo, T. Jiao, Q. Zhang, W. Guo, Q. Peng, X. Yan, "Preparation of graphene oxide-based hydrogels as efficient dye adsorbents for wastewater treatment", *Nanoscale Res. Lett.*, 10 (2015), pp. 1–10
 - [7] M.Y. Nassar, I.S. Ahmed, "Hydrothermal synthesis of cobalt carbonates using different counter ions: an efficient precursor to nano-sized cobalt oxide (Co₃O₄)", *Polyhedron*, 30 (2011), pp. 2431–2437
 - [8] R. Xing, T. Jiao, Y. Liu, K. Ma, Q. Zou, G. Ma, X. Yan, "Co-assembly of graphene oxide and albumin/photosensitizer Nanohybrids towards enhanced photodynamic therapy", *Polymer*, 8 (2016), p. 181
 - [9] R. Xing, K. Liu, T. Jiao, N. Zhang, K. Ma, R. Zhang, Q. Zou, G. Ma, X. Yan, "An injectable self-assembling collagen-gold hybrid hydrogel for combinatorial antitumor photothermal/photodynamic therapy", *Adv. Mater.*, 28 (2016), pp. 3669–3676
 - [10] Patil R.S, Kokate M.R, Kolekar S.S, *Spectrochimica Acta A*, 2012, 91, 234–238.
 - [11] A.-N.M. Salem, M.A. Ahmed, M.F. El-Shahat, "Selective adsorption of amaranth dye on Fe₃O₄/MgO nanoparticles", *J. Mol. Liq.*, 219 (2016), pp. 780–788.
 - [12] M.E. Olya, M. Vafaei, M. Jahangiri "Modeling of acid dye decolorization by TiO₂-Ag₂O nano-photocatalytic process using response surface methodology", *Journal of Saudi Chemical Society* (2015).
 - [13] Vinodgopal, K., Darrel E. Wynkoop, and Prashant V. Kamat. "Environmental photochemistry on semiconductor surfaces: photosensitized degradation of a textile azo dye, acid orange 7, on TiO₂ particles using visible light." *Environmental Science & Technology* 30.5 (1996): 1660-1666.
 - [14] Nasr, Chouhaid, et al. "Environmental photochemistry on semiconductor surfaces. Visible light induced degradation of a textile diazo dye, naphthol blue black, on TiO₂ nanoparticles." *The Journal of Physical Chemistry* 100.20 (1996): 8436-8442.
 - [15] Zhang, Shunli, et al. "Morphological structure and physicochemical properties of nanotube TiO₂." *Chinese Science Bulletin* 45.16 (2000): 1533-1536.
 - [16] Moreira, Regina de Fátima Peralta Muniz, et al. "Mass transfer and photocatalytic degradation of leather dye using TiO₂/UV." *Journal of applied electrochemistry* 35.7-8 (2005): 821-829.
 - [17] Liu, Shengwei, Jiaguo Yu, and MietekJaroniec. "Tunable photocatalytic selectivity of hollow TiO₂ microspheres composed of anatasepolyhedra with exposed {001} facets." *Journal of the American Chemical Society* 132.34 (2010): 11914-11916.
 - [18] Zhou, Weijia, et al. "Ag₂O/TiO₂ nanobeltsheterostructure with enhanced ultraviolet and visible photocatalytic activity." *ACS applied materials & interfaces* 2.8 (2010): 2385-2392.
 - [19] Kar, Archana, York R. Smith, and Vaidyanathan Subramanian. "Improved photocatalytic degradation of textile dye using titanium dioxide nanotubes formed over titanium wires." *Environmental science & technology* 43.9 (2009): 3260-3265.
 - [20] Jiang, Xin, and Ting Wang. "Influence of preparation method on morphology and photocatalysis activity of nanostructured TiO₂." *Environmental science & technology* 41.12 (2007): 4441-4446.
 - [21] Poursaberi, Tahereh, and MostafaHassanisadi. "Magnetic Removal of Reactive Black 5 from Wastewater Using Ionic Liquid Grafted-Magnetic Nanoparticles." *CLEAN–Soil, Air, Water* 41.12 (2013): 1208-1215.
 - [22] Venkatesha, T. G., Y. ArthobaNayaka, and B. K. Chethana. "Adsorption of Ponceau S from aqueous solution by MgO nanoparticles." *Applied Surface Science* 276 (2013): 620-627.
 - [23] Kannusamy, Pandiselvi, and ThambiduraiSivalingam. "Synthesis of porous chitosan–polyaniline/ZnO hybrid composite and application for removal of reactive orange 16 dye." *Colloids and Surfaces B: Biointerfaces* 108 (2013): 229-238.
 - [24] Xu, Piao, et al. "Synthesis of iron oxide nanoparticles and their application in Phanerochaetechrysosporium immobilization for Pb (II) removal." *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 419 (2013): 147-155.
 - [25] Rahmani, A. R., et al. "Degradation of Azo Dye Reactive Black 5 and acid orange 7 by Fenton-like mechanism." *Iranian Journal of Chemical Engineering* 7.1 (2010): 87-94.
 - [26] Liu, Jinshui, Shi Ma, and LingjieZang. "Preparation and characterization of ammonium-functionalized silica nanoparticle as a new adsorbent to remove methyl orange from aqueous solution." *Applied Surface Science* 265 (2013): 393-398.
 - [27] Saha, Bedabrata, et al. "Preferential and enhanced adsorption of different dyes on iron oxide nanoparticles: a comparative study." *The Journal of Physical Chemistry C* 115.16 (2011): 8024-8033.
 - [28] Mahmoodi, Niyaz Mohammad. "Synthesis of amine-functionalized magnetic ferrite nanoparticle and its dye removal ability." *Journal of Environmental Engineering* 139.11 (2013): 1382-1390.
 - [29] Ahmad, Rais, and Rajeev Kumar. "Adsorption studies of hazardous malachite green onto treated ginger waste." *Journal of environmental management* 91.4 (2010): 1032-1038.
 - [30] Saharan, Priya, et al. "Ultra fast and effective treatment of dyes from water with the synergistic effect of Ni doped ZnO nanoparticles and ultrasonication." *Ultrasonicssono chemistry* 22 (2015): 317-325.
 - [31] Dalvand, Arash, et al. "Dye removal, energy consumption and operating cost of electrocoagulation of textile wastewater as a clean process." *Clean–Soil, Air, Water* 39.7 (2011): 665-672.
 - [32] Lin, Chia-Chang, and Wen-Tzong Liu. "Ozone oxidation in a rotating packed bed." *Journal of Chemical Technology and Biotechnology* 78.2-3 (2003): 138-141.
 - [33] Sharma, Sandeep Kumar, HaripadaBhunia, and Pramod Kumar Bajpai. "Photocatalyticdecolorization kinetics and mineralization of reactive black 5 aqueous solution by UV/TiO₂ nanoparticles." *CLEAN–Soil, Air, Water* 40.11 (2012): 1290-1296.
 - [34] Mahmoodi, Niyaz Mohammad, JafarAbdi, and DariushBastani. "Direct dyes removal using modified magnetic ferrite nanoparticle." *Journal of Environmental Health Science and Engineering* 12.1 (2014): 1.
 - [35] Mahmoodi, Niyaz Mohammad, et al. "Decolorization and mineralization of textile dyes at solution bulk by heterogeneous nanophotocatalysis using immobilized nanoparticles of titanium dioxide." *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 290.1 (2006): 125-131.
 - [36] Salehi, Raziye, et al. "Novel biocompatible composite (chitosan–zinc oxide nanoparticle): preparation, characterization and dye adsorption properties." *Colloids and Surfaces B: Biointerfaces* 80.1 (2010): 86-93.
 - [37] Ghaedi, Mehrorang, et al. "Comparison of silver and palladium nanoparticles loaded on activated carbon for efficient removal of Methylene blue: Kinetic and isotherm study of removal process." *Powder Technology* 228 (2012): 18-25.
 - [38] Kumar, K. Yogesh, et al. "Low-cost synthesis of metal oxide nanoparticles and their application in adsorption of commercial dye and heavy metal ion in aqueous solution." *Powder technology* 246 (2013): 125-136.
 - [39] Tan, KahAik, et al. "Removal of cationic dye by magnetic nanoparticle (Fe₃O₄) impregnated onto activated maize cob powder and kinetic study of dye waste adsorption." *APCBEE Procedia* 1 (2012): 83-89.
 - [40] Cao, Chunhua, et al. "In situ preparation of magnetic Fe₃O₄/chitosan nanoparticles via a novel reduction–precipitation method and their application in adsorption of reactive azo dye." *Powder Technology* 260 (2014): 90-97.
 - [41] Basturk, Emine, and Mustafa Karatas. "Decolorization of antraquinone dye Reactive Blue 181 solution by UV/H₂O₂ process." *Journal of photochemistry and Photobiology A: Chemistry* 299 (2015): 67-72.
 - [42] Ahmad, Rais, and Rajeev Kumar. "Adsorption of amaranth dye onto alumina reinforced polystyrene." *CLEAN–Soil, Air, Water* 39.1 (2011): 74-82.
 - [43] Fan, Lulu, et al. "Fabrication of magnetic chitosan nanoparticles grafted with β -cyclodextrin as effective adsorbents toward hydroquinol." *Colloids and Surfaces B: Biointerfaces* 95 (2012): 42-49.
 - [44] Mukhopadhyay, Arka, Anjan Kumar Dasgupta, and KrishanuChakrabarti. "Thermostability, pH stability and dye degrading activity of a bacterial laccase are enhanced in the presence of Cu₂O nanoparticles." *Bioresource technology* 127 (2013): 25-36.
 - [45] Khataee, A. R., et al. "Biological treatment of a dye solution by MacroalgaeChara sp.: Effect of operational parameters, intermediates identification and artificial neural network modeling." *Bioresource technology* 101.7 (2010): 2252-2258.